Removal of Benzothiophene Using Butylmethylimidazolium Tetrachloroferrate [BMIM][$FeCl_4$] Ionic Liquid from Dodecane Model Oil

by

Karimah Aminudin

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

DECEMBER 2009

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Removal of Benzothiophene Using Butylmethylimidazolium Tetrachloroferrate [BMIM][$FeCl_4$] Ionic Liquids from Dodecane Model Oil

by

Karimah Aminudin

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

_____
Dr. Chong Fai Kait
Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

November 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____

KARIMAH AMINUDIN

ACKNOWLEDGEMENT

I wish to take the opportunity to express my utmost gratitude to the individuals that had taken the time and effort to assist me in completing the project. Without the cooperation of these individuals, no doubt I would have faced some complications throughout the course. First and foremost my deep and sincere gratitude goes to my supervisor, Dr Chong Fai Kait for giving a chance for me to work under her supervision in completing the project. This project will not successfully complete without her assistance, guidance, encouragement, continuous support and patience. Besides, I would like to show my gratitude to all research officers of Ionic Liquid Department, Universiti Teknologi PETRONAS especially to Ms. Siti Hawatulaila for providing me with all the information required to begin the project and assisting me in conducting experiments in the laboratory. I am indebted to my many of my colleagues for providing stimulating and fun environment in which to learn and grow. Their support, advice and extensive discussion have been very helpful for completing this project. Last but not least, I owe my deepest gratitude to my beloved family for their understanding and moral support to motivate and allowed me to pursue to greater heights in my studies. To all individuals who helped me in any way, but whose name was not mentioned here, I thank you to all from the bottom of my heart.

ABSTRACT

Sulfur compound is the key substance that needs to be separated from model oil. The conventional sulfur compound removing method is catalytic hydrodesulfurization (HDS), which requires both a high temperature and high pressure of hydrogen gas to produce oil having low levels of sulfur compounds. Therefore, the efficiency of HDS is limited in treating benzothiophene. This project is to develop an advanced desulfurization process that can be carried out under mild conditions; atmospheric pressure and room temperature. Extractive desulfurization using [BMIM][$FeCl_4$] ionic liquid was investigated to remove benzothiophene from dodecane model oil. The objective is to synthesize [BMIM][$FeCl_4$] ionic liquid and determine its performance in desulfurization of model oil. Project scope involved mainly four stages; synthesis of the [BMIM][$FeCl_4$] ionic liquid, characterization of ionic liquid using NMR and FTIR, extraction of benzothiophene from dodecane model oil, (containing 4% and 6% benzothiophene) and determination of sulfur removal efficiency using CHNS analyzer. Two ionic liquids were prepared using anhydrous $FeCl_3$ and hexaydrates $FeCl_3$ reacted with butylmethylimidazolium chloride. Sulfur removal efficiency of [BMIM][$FeCl_4$] ionic liquid prepared from anhydrous $FeCl_3$ is 88.6% compared to from hexahydrates $FeCl_3$ which is 87.9% for 4.0% benzothiophene in dodecane. The ionic liquid performance decreases as the percentage of sulfur increases.

.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

[BMIM][$FeCl_4$]	Butylmethylimidazolium tetrachloroferrate
[BMIM]Cl	1-Butyl-3-Methylimidazolium Chloride
CHNS	Carbon Hydrogen Nitrogen Sulfur
$FeCl_3$	Ferric Chloride
FTIR	Fourier Transformer Infrared
H_2S	Hydrogen Sulfide
HDS	Hydrodesulfuriaztion
LLE	Liquid-Liquid Extraction
NMR	Nuclear Magnetic Resonance
ppm	Parts Per Million
RTIL	Room Temperature Ionic Liquid
SO_2	Sulfur Dioxide
VOC	Volatile Organic Compound

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Sulfur removal from crude oil becomes an increasingly important challenge in refinery industry. Catalytic hydrogenation is the conventional process for crude oil desulfurization. There is an increased interest in alternative processes to the current state of the art, HDS, for removing sulfur-containing compounds in refineries. This paper critically discusses the non-HDS process for liquids fuels which is using ionic liquids technology. Since the early 1990s, there has been a growing interest in expanding ionic liquids to widespread applications in which ionic liquid promises an environmental friendly reaction in crude oil desulfurization. Current study found that the use of microwave synthesis has considerably speed up ionic liquid synthesis, as well as making their synthesis a model in green chemistry, being stoichiometric, atom economic, and quantitative. Thus the ionic liquids technology is now becoming an important alternative for desulfurization in refinery industry.

The ionic liquid technology is practicing the liquid-liquid extraction (LLE) for desulfurization of crude oil. LLE also known as solvent extraction and partitioning, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. It is an extraction of a substance from one liquid phase into another liquid phase. LLE is a basic technique in chemical laboratories, where it is performed using a separatory funnel. This type of process is commonly performed after a chemical reaction as part of the work-up.

Ionic liquids as selective extraction agents of sulfur compounds is discussed because of their novelty and theoretical interest. Provisionally, the best results were obtained with $AlCl_3$-1-butyl-3-methylimidazolium chloride (BMIM/$AlCl_4$) researched by Bosman and friends, 2002 but the desulfurization rate was not high (85%). Deep desulfurization using a chlorine-free ionic liquid (anion is octylsulfate and cation N-octyl-N-methylimidazolium) was also studied. This agent is not sensitive to water compared to

aluminium complexes. A lot of studies had been done for a range of ionic liquids with varying cation classes and a range of anion types to remove organic sulfur in crude oil model. This project investigates the extraction efficiency enhancement for the desulfurization using butylimidazolim chloride, BMIMCl with addition of metal halide, $FeCl_3$.

1.2 Problem Statement

The significance of ionic liquids has gained rising attention over the past years due to its unique properties both as extractant and also as catalyst especially in desulfurization of crude oil model. The classical desulfurization process involves catalytic hydrogenation of sulfur compounds HDS into hydrogen sulfide. However, several concerns come up in corresponding to the conventional technology. Sulfur-compounds such as dibenzothiophene is less reactive to HDS in which require higher hydrogen consumption and the use of additional infrastructure in the treatment facility. (Rang et al., 2006). In brief, HDS consumed high energy and capital cost. Thus, extraction of benzothiophene from crude oil model using ionic liquids could be an alternative to HDS. The addition of metal halide in ionic liquid is the focus subject in this project since it is a new innovation going to be applied in desulfurization process.

1.3 Objective and Scope of Study

The objective of this project is to determine the benzothiophene removal efficiency by [BMIM][$FeCl_4$] ionic liquid from crude oil models. The project deals mainly with desulfurization process using metal halide addition in ionic liquids.

The scope of study for this project involves:

- Synthesis of [BMIM][$FeCl_4$] ionic liquid
- Comparison of the efficiency of metal halide addition in ionic liquid with different percentage of benzothiophene in dodecane
- Determining the water content of the [BMIM][$FeCl_4$] ionic liquid

CHAPTER 2
LITERATURE REVIEW

2.1 Ionic Liquid Overview

Ionic liquid is a liquid that contains essentially only ions. Some ionic liquids, such as ethylammonium nitrate are in a dynamic equilibrium where at any time more than 99.99% of the liquid is made up of ions rather than molecular species. In the broad sense, the term includes all molten salts, for instance, sodium chloride at temperatures higher than 800 °C. Today, however, the term "ionic liquid" is commonly used for salts whose melting point is relatively low (below 100 °C). In particular, the salts that are liquid at room temperature are called room-temperature ionic liquids, or RTILs. There also exist mixtures of substances which have low melting points, called Deep eutectic solvent, or DES, that have many similarities with ionic liquids. (Murugesana et al., 2005).

Within the last twenty years, research involving these unique liquids has grown exponentially. Nowadays, ionic liquids find a number of industrial applications which vary greatly in character. Ionic liquids have shown potential as green solvents, electrochemical agents, lubricants and compressor fluids. As more and more ionic liquids are being manufactured, it is often difficult to obtain physical and chemical data needed to perform feasibility tests.

The reasons why ionic liquid is considered in this study because:

- Ionic liquids are environmentally-friendly alternatives to organic solvents for liquid-liquid extractions, catalysis, separations, and electrochemistry.
- Ionic liquid will reduce or eliminate the related costs, disposal requirements, and hazards associated with volatile organic compounds (VOCs).
- The ability to fine-tune the properties of the ionic liquid medium will allow selection of ionic liquid to replace specific solvents in a variety of different processes.

2.2 Characteristic of Ionic Liquid

Ionic liquids are room-temperature salts composed entirely of ions and have wide liquid temperature range as been mentioned previously. They have several important properties such as wide electrochemical window, extremely low volatility, nonflammability, corrosion resistance to plastics and carbon steels, high thermal stability, high ionic conductivities and high solvating capability. Variations in cations and anions can produce a large number of ionic liquids. Properties of ionic liquid depend on the structure of ions.

Ionic liquids are electrically conductive and have extremely low vapor pressure. (Their noticeable odours are likely due to impurities.) Their other properties are diverse. Many have low combustibility, excellent thermal stability, a wide liquid range, and favorable solvating properties for diverse compounds. Many classes of chemical reactions, such as Diels-Alder reactions and Friedel-Crafts reactions, can be performed using ionic liquids as solvents.

Despite their extremely low vapor pressures, some ionic liquids can be distilled under vacuum conditions at temperatures near 300 °C. Some ionic liquids (such as 1-butyl-3-methylimidazolium nitrate) generate flammable gases on thermal decomposition. Thermal stability and melting point are dependent on the components in the liquid. (Ko et al., 2008).

The solubility of different species in imidazolium ionic liquids depends mainly on polarity and hydrogen bonding ability. Simple aliphatic compounds are generally only sparingly soluble in ionic liquids, whereas olefins show somewhat greater solubility, and aldehydes can be completely miscible. This can be exploited in biphasic catalysis, such as hydrogenation and hydrocarbonylation processes, allowing for relatively easy separation of products and/or unreacted substrate(s). Gas solubility follows the same trend, with carbon dioxide gas showing exceptional solubility in many ionic liquids, carbon monoxide being less soluble in ionic liquids than in many popular organic solvents, and hydrogen being only slightly soluble (similar to the solubility in water)

and probably varying relatively little between the more popular ionic liquids. (Different analytical techniques have yielded somewhat different absolute solubility values). (Leffler, 2008)

Chemical structure for ionic liquid as shown in figure below:

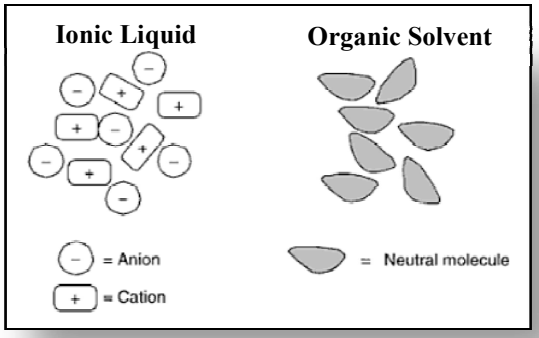


Figure 2.1: Comparison of the Structures of an Ionic Liquid and an Organic Solvent. In The Ionic Liquid, Cations Are Solvated by Anions and Vice Versa

2.3 Sulfur Content

Sulfur is chemically bonded to some of the more complicated hydrocarbon molecules so that it is not easily separated from the pure carbon compounds. That is, not until it is burned. Then, it will form one of several smelly or otherwise environmentaly objectionable sulfur/oxygen compounds. So sulfur removal before hydrocarbons ever get to the burner tip remains a big issue for refiners today and will be the subject of more words later on. Removal of sulfur from crude oil is believed to be efficiently eliminated by using ionic liquids which are environmental friendly.

The phrasing in discussing crude oils of varying sulfur content is to categorize them into sweet crudes and sour crudes. Today, sweet crudes typically have 0.5% sulfur content or less, sour 0.5% or more. The area in between is sometimes called intermediate sweet or intermedieate sour, but the distinction is not clear.

State of the art in desulfurization technology is HDS which converted sulfur compound to H_2S. Typical reaction conditions are 350^oC and 30-100 bar hydrogen pressure, requiring high pressure reactor and vessel, and thus high investment costs. (Eber et al., 2004).

Extraction of sulfur compounds from gasoline and diesel oil by ionic liquids indicates that such a process could be an alternative to common HDS for deep desulfurization down to values of 10 ppm sulfur or even lower. The results show the selective extraction properties of ILs, especially with regard to those sulfur compounds which are hard to remove by HDS, *e.g.* benzothiophene and dibenzothiophene in Figure 2.2 derivatives present in middle distillates like diesel oil. (Eber et al., 2004).

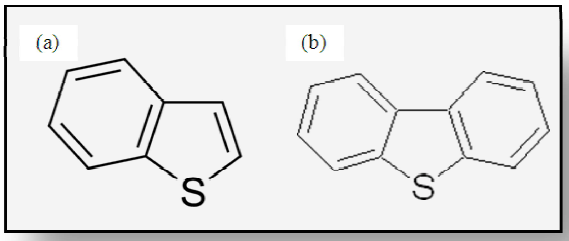


Figure 2.2: Aromatic Organic Compound (a) Benzothiophene (b) Dibenzothiophene

2.4 Extractive Desulfurization Using Fe-Containing Ionic Liquid

Butylmethylimidazolium tetrachloroferrate [BMIM][$FeCl_4$] is a kind of ionic liquid and also been known as a magnetic ionic liquid. Magnetic ionic liquid has the unusual properties of ionic liquids. Besides, they show strong response to magnetic field. (Song et al., 2008) Based on the reading, recently, the $FeCl_4^-$ moiety could play roles as synthetic catalyst as well as a dopant when polymerization of π-conjugated polymer was conducted in [BMIM][$FeCl_4$].

The reason that ionic liquids can be used in desulfurization may be that molecules with highly polarizable π- electron density (such as thiophene) preferably insert into the dynamic structure of the ionic liquids, and the driving force for the molecular insertion

is the favorable electronic interaction of polarized aromatic molecules with the charged ion pairs of ionic liquids. (Yu-Xin et al., 2005).

A group of researchers has developed a novel solid electrolyte in which an ionic liquid is confined in a network polymer called "ion gel". This ion gel is expected to contribute to solidification of various electrochemical systems and safety improvement as it exhibits exceedingly high ion-conductivity compared with conventional solid polymer electrolytes. Recently, Hamaguchi and co-workers reported that 1-butyl-3-methylimidazolium tetrachloroferrate is a magnetic ionic liquid. The new magnetic ionic liquid overcomes various problems of traditional magnetic fluids, and is expected to be applied to many fields. (Tokyo Chemical Industry, 2009).

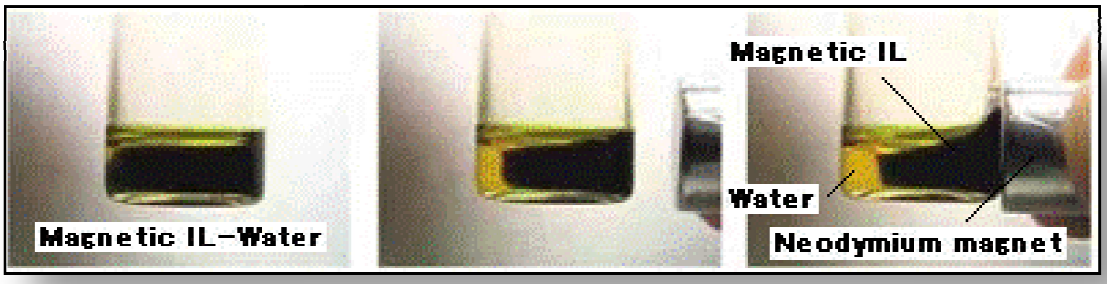


Figure 2.3: Fe-Containing Ionic Liquid Give Response to Magnetic Field

2.4.1 Degree of Desulfurization

Table 2.1 below shows the degree of desulfurization at diferrent molar ratio of $FeCl_3$:[BMIM]Cl. As can be seen, the best molar ratio for 100% sulfur removal is in the range of 2-5. (Ko et al., 2008).

The extraction of DBT was conducted at room temperature with the model oil containing 5000 ppm of DBT and 20000 ppm of n-octane as an internal standard in n-heptane. The weight ratio of model oil/ionic liquid was set at 5.

Table 2.1: Desulfurization of the Model Oil by [BMIM][$FeCl_4$] at Various Molar Ratios of $FeCl_3$/[BMIM]Cl

Molar Ratio ($FeCl_3$/[BMIM]Cl)	Degree of Desulfurization (%)
[BMIM]Cl only	17.2
0.5	34.1
0.7	38.9
1	42.2
1.5	77.4
2	100
2.5	100
3	100
5	100
$FeCl_3$ only	33.9

Then, the degree of desulfurization of [BMIM][$FeCl_4$] ionic liquid was compared with other type of ionic liquid as shown in Table 2.2.

Table 2.2: Desulfurization of the Model Oil by Various Types of Ionic Liquids

Ionic Liquid[b]	Degree of Desulfurization (%)
$FeCl_3$-[HHIM]Cl	9.6
$FeCl_3$-[HMIM]Cl	11.7
$FeCl_3$-[HDMIM]Cl	18.5
$FeCl_3$-[BMIM]Cl	42.2
$FeCl_3$-[BMIM]Cl[c]	100
$FeCl_3$-[BDMIM]Cl	44.8
$FeCl_3$-[BDMIM]Cl[c]	100
$AlCl_3$-[BMIM]Cl[c]	23.5
CuCl-[BMIM]Cl[c]	17.2
$FeCl_3$-[BMIM]Cl[c,d]	100

[b] Molar ratio of $FeCl_3$/ionic liquid = 1
[c] Molar ratio of metal chloride/ [BMIM]Cl =2.
[d] Diesel oil with a sulfur content of 1180 ppm was used instead of the model oil.

From Table 2.1, the 100% desulfurization occur when molar ratio [BMIM] [$FeCl_4$] from 2 to 5. $FeCl_3$ give 33.9% of sulfur removed. Based on the Table 2.2 above, with molar ratio equal to 2, [BMIM]Cl shows the best type of imidazolium-based ionic liquids with Fe^{III} for 100% desulfurization compare to other anion based ionic liquids. Desulfurization using the ionic liquid [BMIM]Cl alone obtained lower degree of desulfurization. Hence, the addition of $FeCl_3$ helps to increase the performance of ionic liquid to remove sulfur. In addition, the presence of hydrogen atom was not helpful to improve the performance of ionic liquids to extract DBT. As listed in Table 2.2, the ionic liquid with one or two acidic hydrogen atoms on the imidazolium ring exhibited much lower extraction ability than the ionic liquids containing two or three alkyl groups.

Therefore, [BMIM][$FeCl_4$] ionic liquid has higher potential to fully remove sulfur from crude oil in industry. In the oil and gas industry, current issue that challenges the desulfurization is the water content in crude oil. High water content decreases the crude oil production quality.

2.4.2 Comparison Other Ionic Liquid Containing Metal Halide

In particular, Lewis acidic ionic liquids containing metal halide anions, such as $AlCl_4$ and $CuCl_2$ showed promising results on the selective removal of aromatic sulfur compounds even though the extraction was carried out at relatively high temperature around 70^oC because of their inherent low fluidity. (Ko et al., 2008).

Study of the extraction using [BMIM][Cu_2Cl_3] ionic liquid was performed at 80^oC**.** (Huang et al., 2004). The degree of desulfurization was compared with [BMIM][$AlCl_4$] and [BMIM][BF_4]. Result of percentage of sulfur removed by extraction of different ionic liquid was determined as in Table 2.3. The molar ratio of metal halide/ionic liquid is 2 and the mass ratios of ionic liquids to model oil is 1:5.

Table 2.3: Desulfurization of the Model Oil by Extraction with Different Ionic Liquids (Huang et al., 2004)

Ionic Liquid	Degree of Desulfurization (%)
[BMIM][Cu_2Cl_3]	23.4
[BMIM][$AlCl_4$][a]	16.0
[BMIM][BF_4][b]	11.0

[a] Result from Bosmann et al. The extraction was performed at a temperature of 80°C and model oil was prepared by adding dibenzothiophene to n-dodecane.
[b] Result from Akzo Nobel Chemical, Inc. The extraction was performed at room temperature and the model oil was prepared by adding dibenzothiophene and piperdine to n-dodecane.

2.5 Ionic Liquid Characteristic and Performance Analysis

The characteristic of ionic liquid can be study using FTIR analysis. The functional group present in the ionic liquid could be identified using this analysis. Furthermore, water content in ionic liquid could be determined by using Karl Fischer. On the other hand, CHNS analyzer is used to investigate the performance of ionic liquid in removing sulfur from model oil.

2.5.1 Fourier Transformer Infrared (FTIR)

Considering physical and analytical chemistry, infrared spectroscopy (IR spectroscopy) is a technique used to identify functional group present in a chemical compounds based on how infrared radiation is absorbed by the compound's chemical bonds. There is a reference known as IR spectroscopy correlation table that lists some general absorption peaks for common types of atomic bond and functional groups.

2.5.2 Karl Fischer

Karl Fischer is a classic titration method in analytical chemistry that uses coulometric or volumetric titration to determine trace amounts of water in a

sample. Karl Fischer titration is a widely used analytical method for quantifying water content in a variety of products. The fundamental principle behind it is based on the Bunsen reaction between iodine and sulfur dioxide in an aqueous medium. Karl Fischer discovered that this reaction could be modified to be used for the determination of water in a non-aqueous system containing an excess of sulfur dioxide. He used a primary alcohol (methanol) as the solvent, and a base (pyridine) as the buffering agent.

Water and iodine are consumed in a 1:1 ratio in the above reaction. Once all of the water present is consumed, the presence of excess iodine is detected voltametrically by the titrator's indicator electrode. That signals the end-point of the titration. The amount of water present in the sample is calculated based on the concentration of iodine in the Karl Fisher titrating reagent and the amount of Karl Fisher reagent consumed in the titration.

2.5.3 CHNS Analyzer

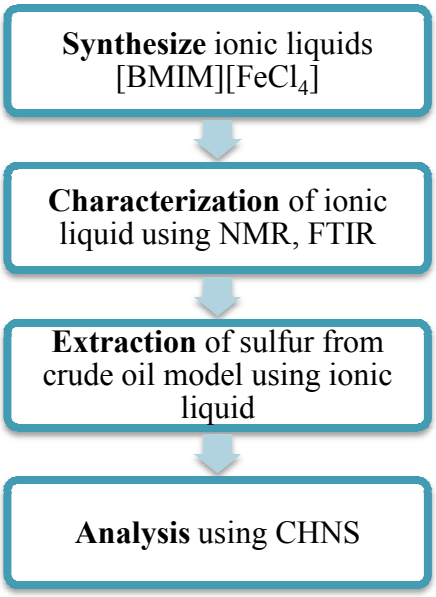
CHNS analyzer is a scientific instrument which can determine the elemental composition of a sample. The name derives from the elements measured by the device: carbon (C), hydrogen (H), nitrogen (N) and sulfur (S). The analyzer uses a combustion process to break down substances into simple compounds which are then measured.

Extraction performance can be analyzed from the CHNS result. The amount of elements measured can be used to calculate the ionic liquid efficiency of sulfur removal from model oil. Therefore, the CHNS result is the most important in this project.

CHAPTER 3
METHODOLOGY

The scope of this project is mainly to determine the efficiency of [BMIM][$FeCl_4$] in removing the benzothiophene from dodecane. First and foremost, the ionic liquid was synthesized by adding the metal halide, ferric chloride [$FeCl_3$] into butymethyllimidazolium chloride [BMIM]Cl. Two different ionic liquid was synthesized; one was [BMIM]Cl with added anhydrous $FeCl_3$ and the other one was [BMIM]Cl with added $FeCl_3.6H_2O$. The synthesized ionic liquids were then gone through characterization stage. Afterward, the ionic liquids were used to remove benzothiophene in dodecane whereby several variables allocated in order to determine the efficiency. The extraction of sulfur from model oil was varied by using 4% and 6% of benzothiophene in dodecane. In addition, dodecane without sulfur containing compounds was also extracted as a reference extraction comparison. Lastly, the percentage of benzothiophene removal was analyzed using CHNS analyzer. The objective to determine efficiency of the synthesized ionic liquid was verified by the percentage of sulfur removal. All the chemicals and equipments for this lab work are listed in Appendix B.

In summary, removal of benzothiophene using ionic liquid from crude oil model consist of four significant stages:



3.1 Synthesis of Ionic Liquid [BMIM][$FeCl_4$]

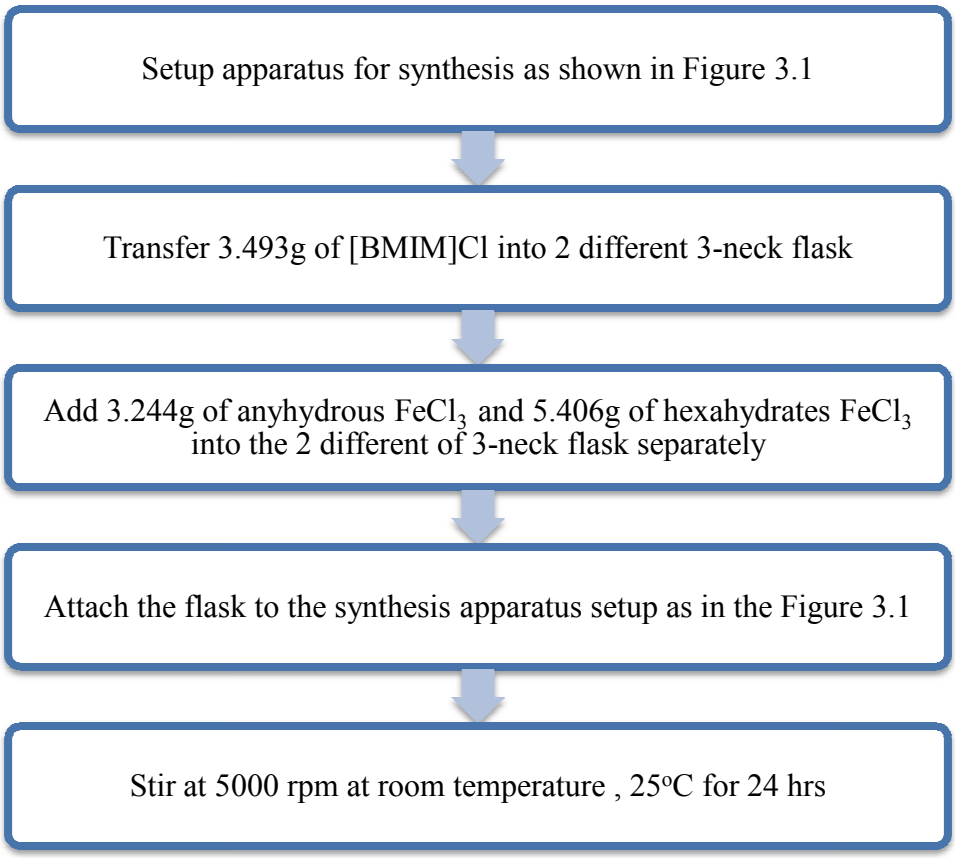


Figure 3.1: Overall View of Synthesis Apparatus Connection

Caution: [BMIM]Cl and $FeCl_3$ could be easily hydrolyse. Thus, glove bag must be used to avoid moisture contamination during the mass preparation.(Figure 3.2)

Figure 3.2: Glove Bag

3.2 Characterization of Ionic Liquid Using NMR, FTIR, & Karl Fischer

Prepare small amount of synthesized ionic liquid in a vial to be sent for NMR analysis. FTIR anlyzer was used to identify the components exist in the synthesized ionic liquid. Besides, the water content in ionic liquid was determined using Karl Fischer.

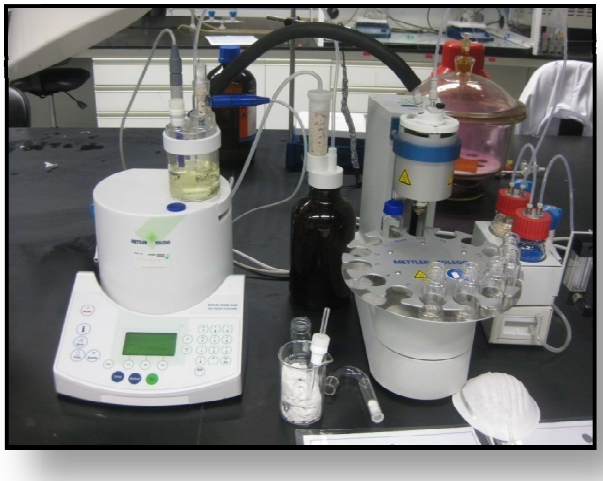


Figure 3.3: Karl Fischer

3.3 Extraction of Benzothiophene from Model Oil Using Ionic Liquid

At first, the extraction was done using 4% of benzothiophene in dodecane for both anhydrous and hexahydrates $FeCl_3$. It was observed from the CHNS analysis that ionic liquid using anhydrous $FeCl_3$ has higher efficiency compared to using $FeCl_3.6H_2O$. Therefore, only anhydrous $FeCl_3$ was used in extraction of 6% benzthiophene in dodecane.

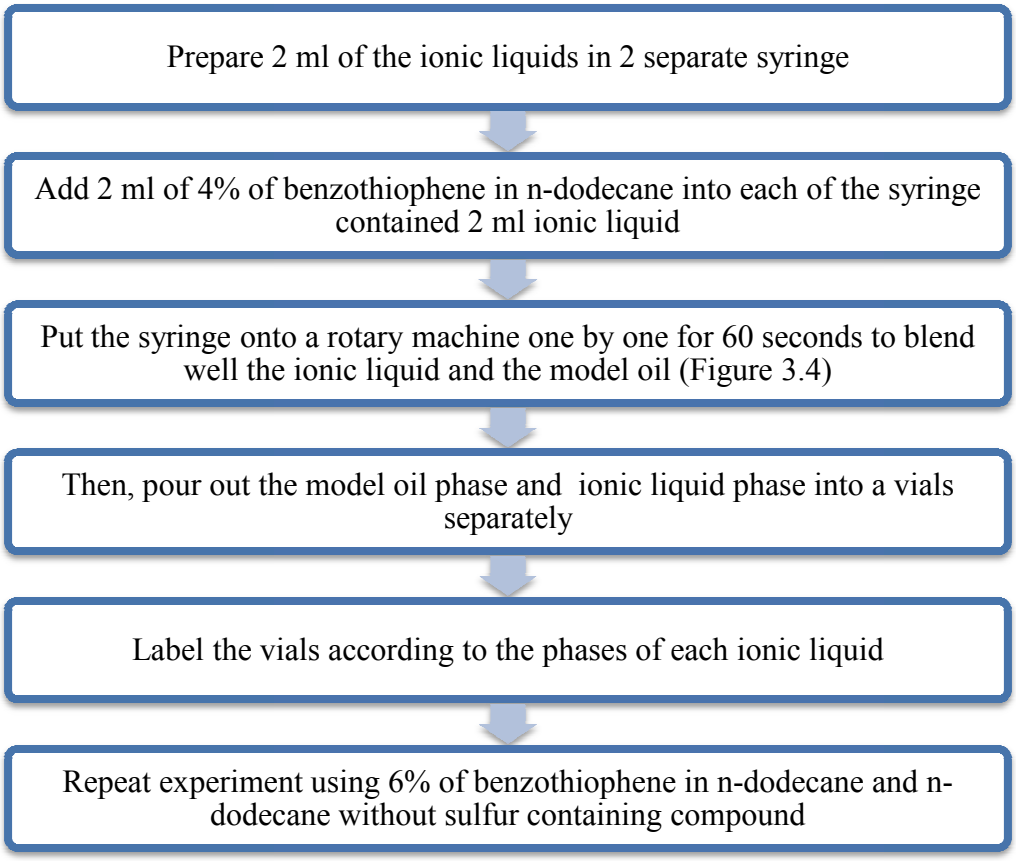


Figure 3.4: Rotary Machine

3.3.1 Photoreaction During Extraction

Identify the reaction occur during the extraction stage during ionic liquid is added into crude oil model.

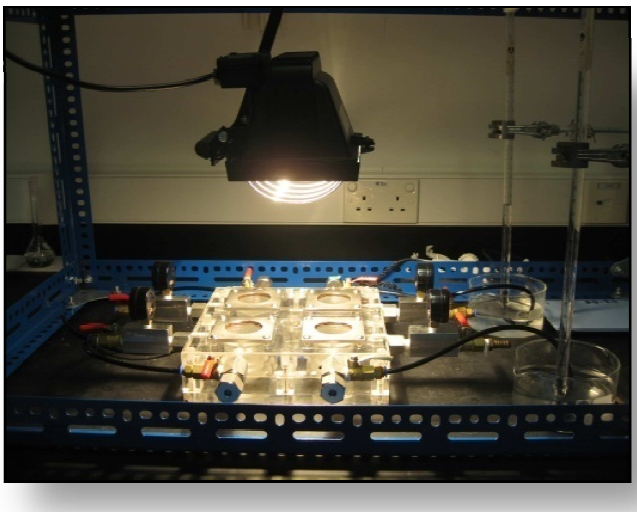


Figure 3.5: Photoreactor for Desulfurization

3.4 Analysis Using CHNS

Samples of model oil after extraction stage were analyzed using CHNS analyzer to determine the percentage of sulfur compound remained.

Figure 3.6: CHNS Analyzer

CHAPTER 4
RESULT AND DISCUSSION

4.1 Synthesis [BMIM][$FeCl_4$] Ionic Liquid

Figure 4.1 and Figure 4.2 show the synthesized ionic liquid using anhydrous and hexahydrate $FeCl_3$. Physically, there was no difference in color as can be seen above, the mixtures were dark brown in color. It became viscous at room temperature after being stirred for 24 hours. Both ionic liquids contained lower water content with approximately 132 ppm from Karl Fischer analysis. Generally, ionic liquid that contains lower water content has an advantage of high efficiency in desulfurization of model oil. In some ionic liquid, water content may disturb the attraction towards sulfur containing compound in model oil and thus, less sulfur could be removed.

Figure 4.1: Anhydrous [BMIM][$FeCl_4$]

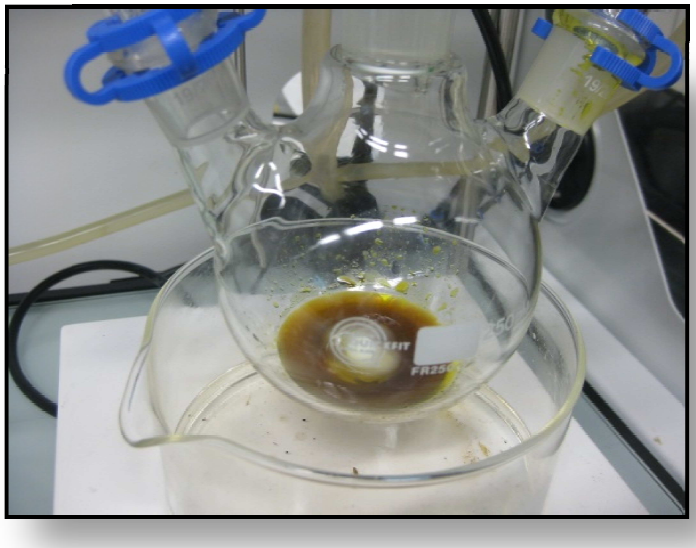


Figure 4.2: Hexahydrates [BMIM][$FeCl_4$]

4.2 NMR Analysis

The result of NMR analysis cannot be determined because of the [BMIM][$FeCl_4$] ionic liquid has magnetic characterization.

4.3 Extraction of Benzothiophene from Model Oil

Clearly can be seen during the experiment, as the model oil was added into the ionic liquid, two layers were formed as in Figure 4.3. It was easy to identify the phases after they were mixed. The upper layer was the model oil and the bottom layer was the ionic liquid phase. Same observation for anhydrous and hexahydrate [BMIM][$FeCl_4$] where the two layers formed during extraction as shown in Figure 4.3 and Figure 4.4. This project involved several variables as mentioned where all the extraction with different benzothiophene content resulted to formed two phases.

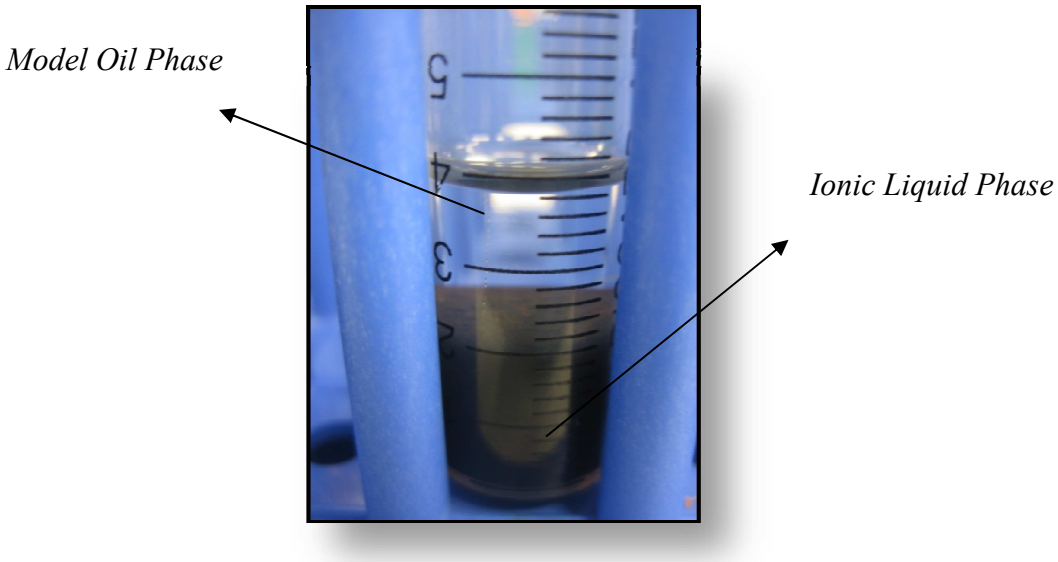


Figure 4.3: Two Layers Formed During Extraction Using Anhydrous [BMIM][$FeCl_4$]

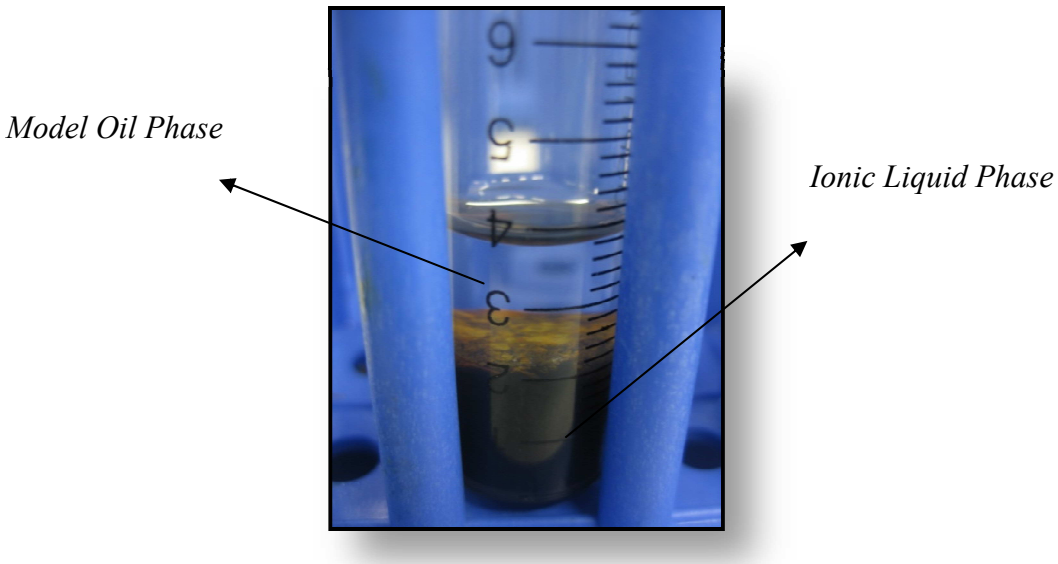


Figure 4.4: Two Layers Formed During Extraction Using Hexahydrate [BMIM][$FeCl_4$]

There was reaction occurred during the two layers formation. Figure 4.5 below shows gas bubbles evolved. It is believed that, the benzothiophene in model oil was extracted by [BMIM][$FeCl_4$] ionic liquid during the extraction stage and released in form of gas bubbles. Reaction was observed immediately as ionic liquid was added to the model oil. After few minutes, the ionic liquid solidifies with traces of yellow powder. The model oil was taken out in a separate vial for CHNS analysis in order to determine the remaining sulfur percentage and the removed sulfur can be calculated.

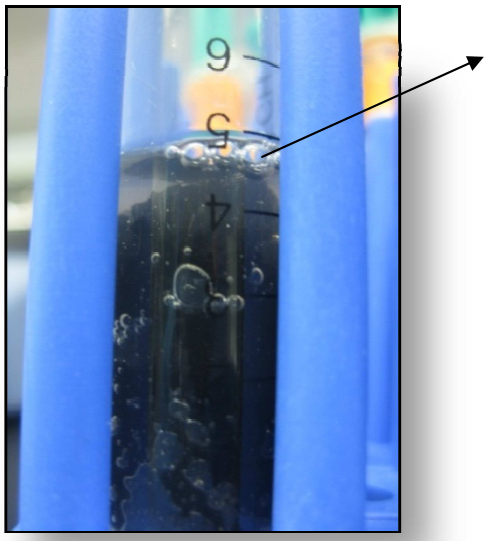


Figure 4.5: Gas Bubble Formed During Extraction Stage

Figure 4.6: Ionic Liquid Solidified After Mixed with Model Oil

4.3.1 Reaction Observation

Halogen lamp was used to initiate the reaction that occurred. A simple procedure was done with two different ways of mixing. At first, ionic liquid was added to a container that contains model oil. Meanwhile, for the second container, model oil was added into ionic liquid. After a few second, there was no reaction in the first container and the ionic liquid was not well mixed with the model oil as shown in Figure 4.7.

For the second container, the mixture was well mix as shown in Figure 4.8. As in extraction stage, the ionic liquid solidified. Thus, oxidation reaction occurred as gas bubble was formed. The gas bubble flowed through a tube to the measuring cylinder to determine the amount of gas formed. The gas formed was calibrated as Table 4.1.

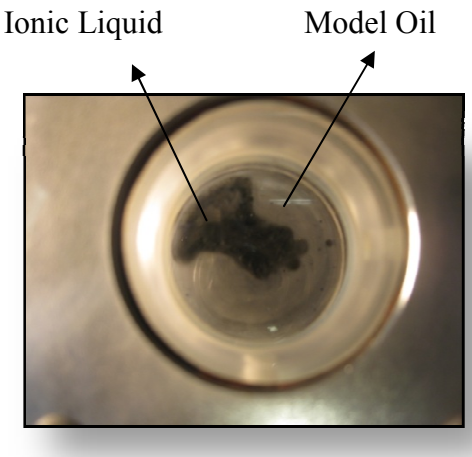


Figure 4.7: Mixture of Ionic Liquid and Model Oil

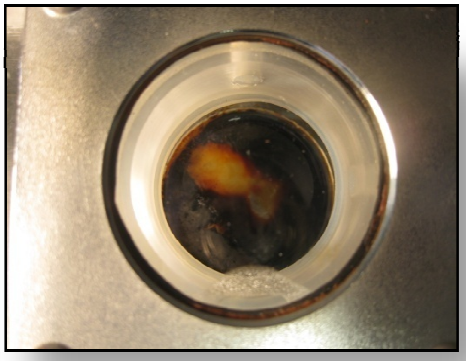


Figure 4.8: Well Mixed of Mixture of Ionic Liquid and Model Oil

Time was recorded as the gas bubble was observed to formed and going upward of the measuring cylinder.

Table 4.1: Time Taken For Each Bubble to Form

Time (s)	Volume (ml)
54	13.7
67	13.8
56	13.9
80	14.0
100	14.2
87	14.3
91	14.4
108	14.5
106	14.6
126	14.7

Time (s)	Volume (ml)
115	14.8
120	14.9
126	15.0
200	15.1
157	15.2
243	15.3
243	15.4
312	15.5
271	15.6
283	15.7

At the beginning, the gas bubble took almost one minute or less to form while approaching to one hour, it took longer time. Based on the table above, the reaction rate was reduced as time elapsed. It was assume to be no reaction after one hour mixing. For almost 1 hour, an amount of 3 ml of gas was produced during the reaction.

4.3.2 pH Level Indicator

Gas bubbles evolved were channeled to the distilled water and were checked qualitatively by pH level indicator. The tested pH indicator strip was compared to the pH indicator reference as in Figure 4.9 and 4.10. Initially, the distilled water was neutral with pH 7 as shown in Figure 4.9. The gas dissolved in water. Then, the water contained dissolved gas was tested by the pH indicator strip as shown in Figure 4.10. It indicates that the water is acidic with pH 2.

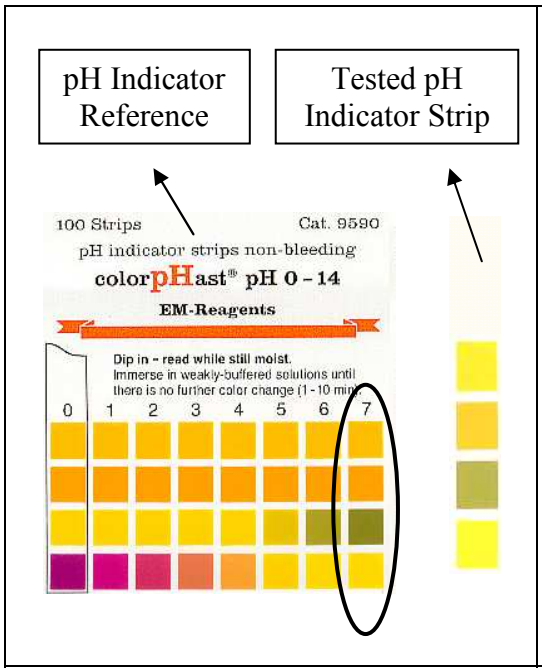


Figure 4.9: Neutral Distilled Water with pH 7

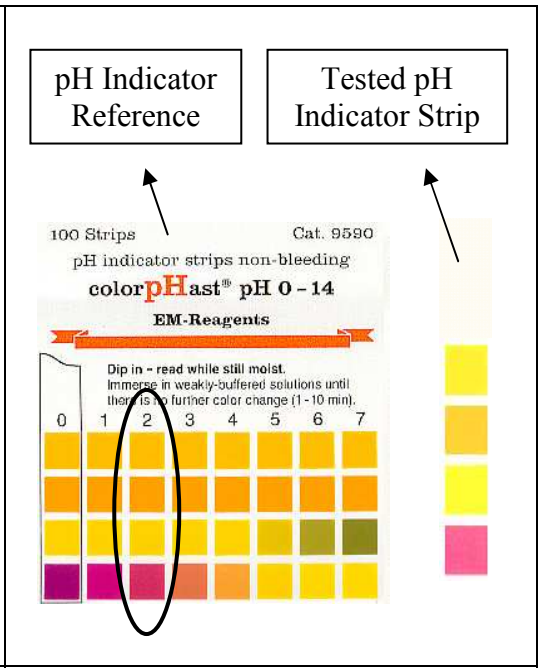


Figure 4.10: Acidic Water Contains Dissolved SO_2 Gas with pH 2

Based on the observation, the gas evolved was slightly white in color. Thus, SO_2 gas was believed has released from the reaction in which it was agreed that sulfur has been removed from the crude oil model.

4.4 FTIR Analysis

FTIR is used to identify chemical compounds based on how infrared radiation is absorbed by the compounds chemical bonds. There is a reference known as infrared spectroscopy correlation table in Appendix F that lists some general absorption peaks for common types of atomic bond and functional groups. FTIR analysis was done for anhydrous [BMIM][$FeCl_4$] ionic liquid because based on the CHNS analysis, the efficiency of desulfurization is higher. Therefore, anhydrous was further experimented for different variables.

Based on Figure 4.9, the valley of the wavenumber indicates the types of the functional group in the ionic liquid for fresh anhydrous [BMIM][$FeCl_4$] ionic liquid which is tends to have the same functional group with anhydrous [BMIM][$FeCl_4$] after extraction as

shown in Figure 4.10. As mentioned in above section, the sulfur has been removed as SO_2 gas released from the reaction. Therefore, the ionic liquid has no changes in chemical compound before and after extraction stage.

The structure of [BMIM][$FeCl_4$] has the interactions between Cl and H atoms as represent by [EMIM][$FeCl_4$] structure in Figure 4.11 . Interaction of aromatic C-H with Cl^- appears in the range of 3000-3100cm^{-1}. (Ko et al., 2008). The FTIR analysis, present alkyl group (wavenumber: 2900-2800cm^{-1}) and amine alkyl group (1200-1025cm^{-1}). Therefore, the analysis illustrate that the [BMIM][$FeCl_4$] is verified.

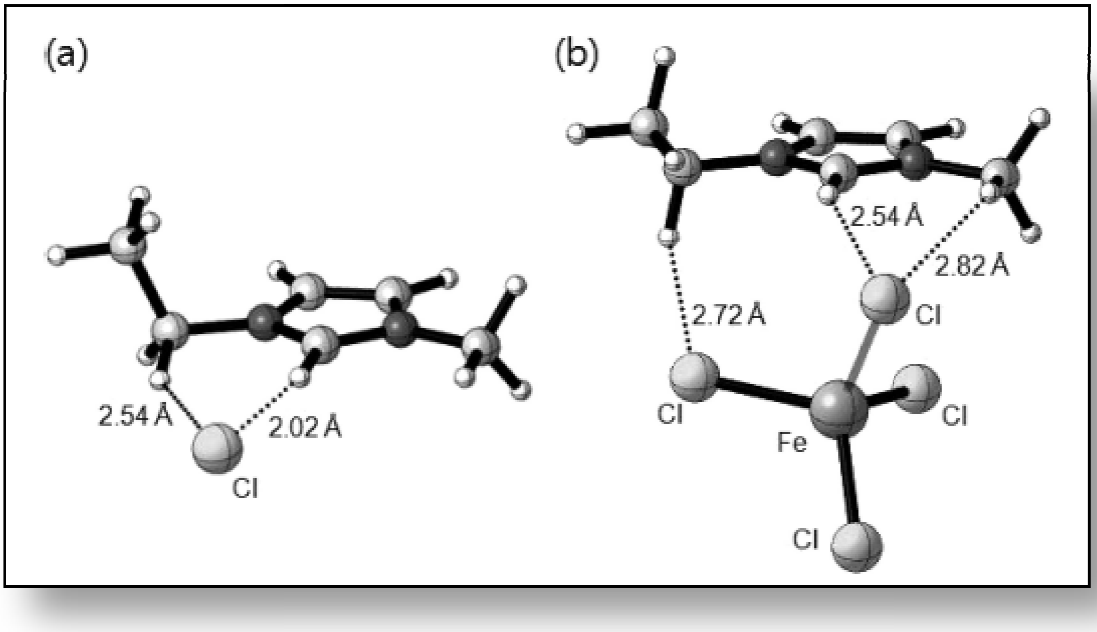


Figure 4.11: Structures of (a) [EMIm]Cl and (b) [EMIm]$FeCl_4$ showing the interactions between Cl and H atoms (Ko et al., 2008)

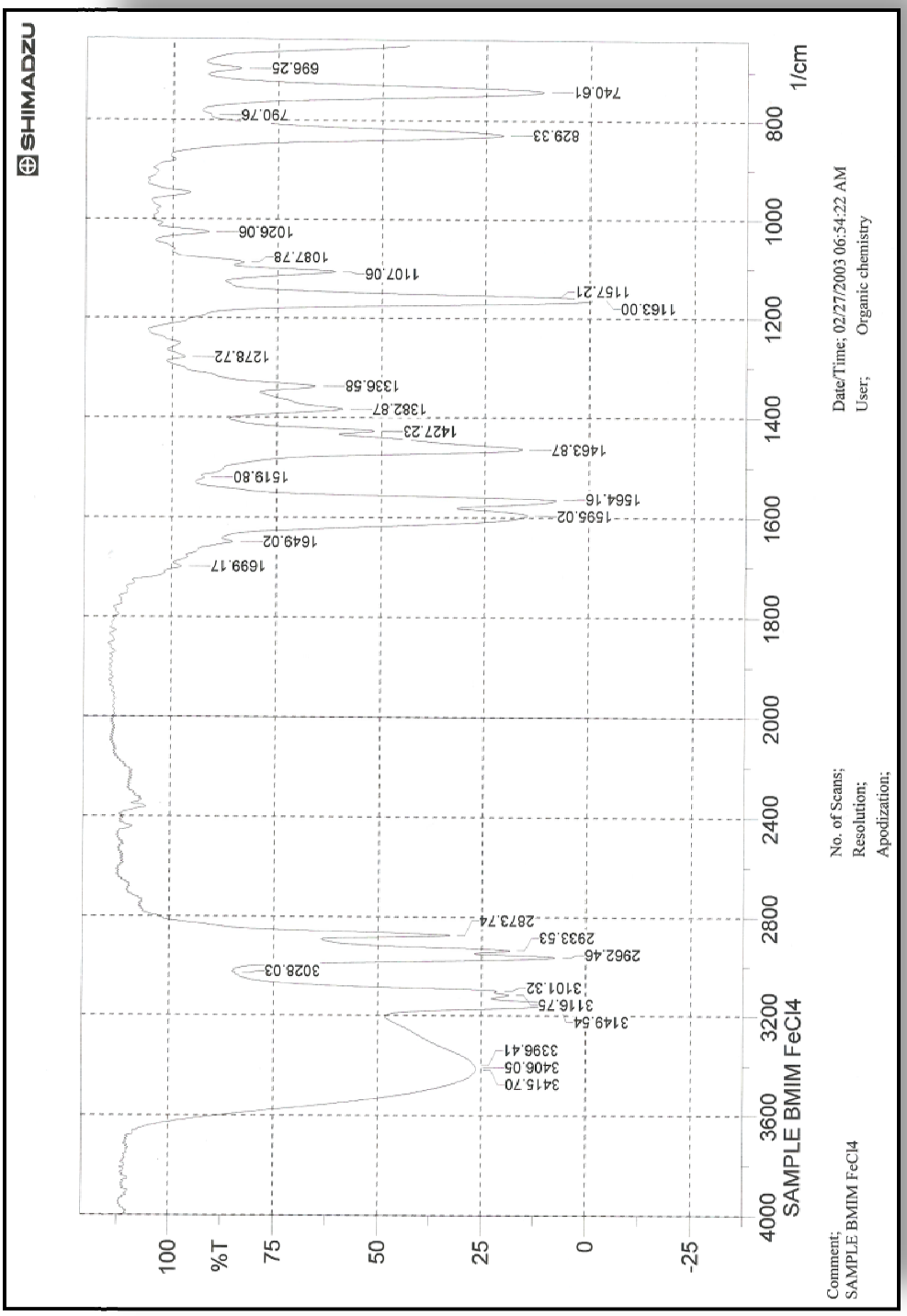


Figure 4.12: FTIR Result for Fresh Anhydrous [BMIM][$FeCl_4$]

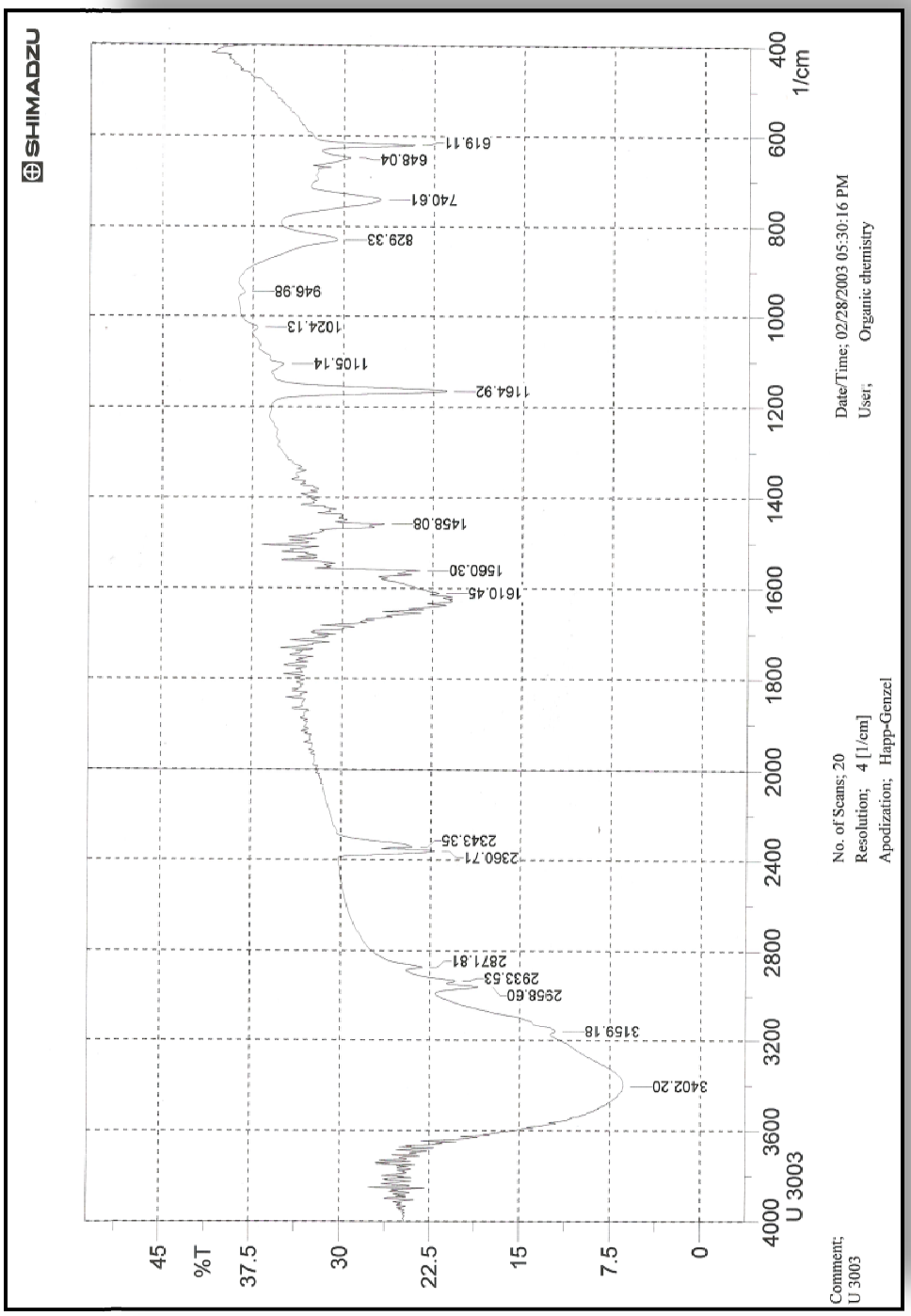


Figure 4.13: FTIR Result for Anhydrous [BMIM][$FeCl_4$]After Extraction

4.5 Ionic Liquid, [BMIM][$FeCl_4$] Efficiency

CHNS analyzer is used to identify the amount of carbon, hydrogen, nitrogen and sulfur components in a chemical mixture. Fresh model oils with different benzothiophene percentage were examined using CHNS analyzer to indicate the initial percentage of sulfur compound. On the other hand, the percentage of sulfur remained in the model oils were examined in order to calculate the amount of sulfur removal.

The initial percentage of sulfur content in the fresh model oils are as listed in the table below:

Table 4.2: Initial Percentage of Sulfur Content in Fresh Model Oil

Component	Initial Sulfur Content (%)
4% of Benzothiophene in dodecane	3.125
6% of Benzothiophene in dodecane	4.932
Dodecane without Benzothiophene content	0.0

The final percentage of sulfur content in the model oils are as listed in the Table 4.3. The percentage of sulfur removal from fresh model oil was calculated by deducting the initial and final percentage of sulfur content in the model oil.

Table 4.3: Remaining and Removal Percentage of Sulfur from Model Oil

Component	Sulfur Remains in Model Oil (%)	Sulfur Removed from Model Oil (%)
4% of benzothiophene in dodecane after extraction with hexahydrates [BMIM][$FeCl_4$]	0.379	2.746
4% of benzothiophene in dodecane after extraction with anhydrous [BMIM][$FeCl_4$]	0.355	2.770
6% of benzothiophene in dodecane after extraction with anhydrous [BMIM][$FeCl_4$]	0.923	4.009
Dodecane without benzothiophene content after extraction with anhydrous [BMim][$FeCl_4$]	0.0	0.0

Efficiency of the ionic liquid is defined by the percentage of sulfur removal in model oil. Generally, it is to identify the ionic liquid performance in removing sulfur.

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial sulfur content (\%)} - \text{Final sulfur content (\%)}}{\text{Initial sulfur content (\%)}} \times 100$$

Thus, the comparisons of ionic liquid efficiency between the different amounts of sulfur content in fresh model oil are simplified as shown in the Table 4.3.

Table 4.4: Ionic Liquid Efficiency

Component	Efficiency (%)
Hexahydrates [BMIM][$FeCl_4$] ionic liquid (4% benzothiophene in dodecane)	87.9
Anhydrous [BMIM][$FeCl_4$] ionic liquid (4% benzothiophene in dodecane)	88.6
Anhydrous [BMIM][$FeCl_4$] ionic liquid (6% benzothiophene in dodecane)	81.3
Anhydrous [BMIM][$FeCl_4$] ionic liquid (Dodecane without benzothiophene content)	0

Based on the result above, the efficiency of anhydrous [BMIM][$FeCl_4$] ionic liquid is slightly higher compare to hexahydrates [BMIM][$FeCl_4$] ionic liquid, 88.6% and 87.9% respectively.

The efficiency of ionic liquid reduces with increasing the percentage of benzothiophene in dodecane. Efficiency of ionic liquid to remove 4% of benzothiophene in dodecane is 88.7% while 6% of benzothiophene in dodecane is 81.3%. The decrease in percentage is still above 80% of efficiency.

Based on the literature review, with molar ratio of ionic liquid and model oil is 1:1; the degree of desulfurization which is the efficiency of the ionic liquid is higher in removing benzothiophene which is this project scope compared with result obtained from Ko et al. (2008) as shown in Table 2.1. The extraction was performed at room

temperature and the model oil was prepared by adding dibenzothiophene to n-octane. The model oil used contained 5000 ppm of dibenzothiophene.

Synthesis of [BMIM][$FeCl_4$] has easier method compared with other ionic liquid such as phosphate based ionic liquid as studied by Nie et al. (2006). The phosphoric ionic liquids were prepared by reacting *N*-methylimidazole and the corresponding trialkyl phosphate at 423 K for 10 h with a yield of 97%. The resulting yellowish viscous liquid was washed three times with diethyl ether at room temperature followed by rotary evaporation under reduced pressure for 12 h to remove all volatile residues. Therefore, synthesis of [BMIM][$FeCl_4$] required less cost and time compared to phosphoric ionic liquid.

From the CHNS anlaysis, the result justified that only sulfur is extracted from the model oil because the amount of carbon, hydrogen, nitrogen and sulfur has no changes by doing the extraction using dodecane without benzothiophene content. Table 4.5 shows the result of CHNS analysis for the dodecane without benzothiophene content.

Table 4.5: Sulfur Content for Dodecane without Benzothiophene Content (%)

Component	Carbon	Hydrogen	Nitrogen	Sulfur
Fresh dodecane without Benzothiophene content (before extraction)	81.10	16.19	0.051	0.0
Final dodecane without Benzothiophene content (after extraction)	81.10	16.19	0.051	0.0

The electronic configuration of Fe^{3+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^0$. According to π-complexation mechanism the cations with empty s-orbitals and the electron density can form the usual σ bonds with their s-orbitals and, in addition, their d-orbitals can back-donate electron density to the anti-bonding π-orbitals of the sulfur rings. Fe^{3+} can form π-complexation bonding with aromatic sulfur compounds. (Gao et al., 2008)

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on the result obtained, [BMIM][$FeCl_4$] ionic liquid could be used as effective extractants for removing benzothiophene compound from dodecane at high efficiency. The degree of desulfurization for extraction using 4% benzothiophene in dodecane is 88.64% by anhydrous [BMIM][$FeCl_4$] ionic liquid while 87.87% by hexahydrates [BMIM][$FeCl_4$] ionic liquid. Besides, the degree of desulfurization for extraction using 6% benzothiophene in dodecane is 81.29% by anhydrous [BMIM][$FeCl_4$] ionic liquid.

As a conclusion, ionic liquid as a 'green chemicals' has high potential to extract sulphur compound from model oil which is cannot be performed by HDS process. The extraction condition using ionic liquid is done at room temperature which is more economical and viable to be practised. Besides, ionic liquid is an environmental-friendly to organic solvents for liquid-liquid extraction and can be regenerated.

5.2 Recommendation

Future implementation may consider to study the effect of water in the ionic liquid for sulfur removal efficiency by exposing the ionic liquid to the air or spiking water into the ionic liquid.

REFERENCES

1. Bica, K., Gaertner, P., Org. Lett. (2006). An Iron-Containing Ionic Liquid as Recyclable Catalyst for Aryl Grignard Cross-Coupling of Alkyl Halides, *Vol. 8,* 733-735.

2. Chen, H., Zhang,W.J., Chen, J.M., Cai, Y.B., Wei Li. A. (2007). Desulfurization of Various Organic Sulfur Compounds and The Mixture of DBT + 4,6-DMDBT by Mycobacterium sp. ZD-19. *Bioresource Technology 99, Elsevier,* 3620-3634.

3. Eber, J., Wasserscheid, P., Jess, A. (2004). Deep Desulfurization of Oil Refinery Streams by Extraction with Ionic Liquids. *Journal of The Royal Society of Chemistry, Vol. 6,* 316-322.

4. Gao, H., Xing, J., Li, Y., Xiong, X., Li, W., Liu, Q., Liu, H. (2008). *Desulfurization of Diesel Fuel by Extraction with Lewis-Acidic Ionic Liquid.* Retrieved from http://aiche.confex.com/aiche/2008/techprogram/P122140.HTM

5. Holbrey, J.D., Lo´pez-Martin, I., Rothenberg, G., Seddon, K.R., Silvero, G., Zheng, X. (2007). Desulfurization of Oils Using ionic Liquids: Selection of Cationic and Ionic Components to Enhance Extraction Efficiency. *Journal of The Royal Society of Chemistry, Vol. 10,* 87-92.

6. Huang, C., Chen, B., Zhang, J., Liu, Z., Li, Y. (2004). Desulfurization of Gasoline by Extraction with New Ionic Liquids. *Energy & Fuels, Vol. 18,* 1862-1864.

7. Ko, N.H, Lee, J. S., Huh E. S., Lee, H., Jung, K.D., Kim, H.S, and Cheong, M. (2008). Extractive DesulfurizationUsing Fe-Containing Ionic Liquid. *Energy & Fuel,Vol. 22,* 1687-1690.

8. Koel, M., Anderson, J.L. (2008). Ionic Liquids in Chemical Analysis. *CRC Press for Taylor and Francis Group,* 273.

9. Leffler, W.L. (2008). *Petroleum Refining in Nontechnical Language, 4th Edition,* 22.

10. Li, H., He, L., Lu, J., Zhu, W., Jiang, X., Wang, Y., Yan, Y. (2008). Deep Oxidative Desulfurization of Fuels Catalyzed by Phosphotungstic Acid in Ionic Liquid at Room Temperature. *Energy & Fuels, Vol. 23,* 1354-1357.

11. Mochizuki, Y., Sugawara. K. (2008). Removal of Organic Sulfur From Hydrocarbon Resources Using Ionic Liquid. *Energy & Fuels, Vol. 22,* 3303-3307.

12. Murugesana, S., Linhardt, R.J. (2005). Ionic Liquids in Carbohydrate Chemistry – Current Trends and Future Directions. *Current Organic Synthesis*, *Vol. 2,* 437-451.

13. Nie, Y., Li, C., Sun, A., Meng, H., and Wang, Z. (2006). Extractive Desulfurization of Gasoline Using Imidazolium-Based Phosphoric Ionic Liquid. *Energy & Fuels, Vol. 20,* 2083-2087.

14. Rang, H., Kann, J., OJA, V. (2004). Advance in Desulfurization Research of Liquid Fuel. *Oil Shale, Vol. 23, No. 2,* 164-176.

15. Song, E.A., Jung, W.G., Ihm, D.W., and Kim, J.Y. (2008). Structural Analysis of Conductive Polypyrroles Synthesized in an Ionic Liquid. *Journal of Bull. Korean Chem. Soc., Vol. 30(5),* 1009-1011.

16. Schmidt, R. (2008). [BMIM]$AlCl_4$ Ionic Liquid for Deep Desulfurization of Real Fuels. *Energy & Fuels, ACS*, 1774-1778.

17. Tokyo Chemical Industry. (2009). *Synthetic Organic Chemistry- Ionic Liquid.* Retrived from http://www.tci-asiapacific.com/product/synthetic-chem/S019.shtml

18. Yu-xin, W., Xin-yong, LI. (2005). Extractive Removal of Thiophene Sulfide from Diesel using Ionic Liquids. *The Proceedings of the 3rd International Conference on Functional Molecules. Department of Environmental Science & Technology, Dalian University of Technology, Dalian 116023, P.R.China,* 273-277

APPENDICES

Appendix A: Gantt Chart

Week/Task	1	2	3	4	5	6	7	8	9		10	11	12	13	14
Project work continue	■	■	■							**Mid-semester break**					
Submission of Progress Report 1				●											
Project work continue				■	■	■	■	■	■						
Submission of Progress Report 2								●							
Seminar								●							
Project work continue											■	■	■	■	
Poster exhibition											●				
Submission of Project Dissertation (soft bound)															●
Oral Presentation											**24/11 – 4/12/2009**				
Submission of Project Dissertation (hard bound)											**7 days after oral presentation**				

●	Suggested Milestones
■	Process

Appendix B: Chemicals and Equipments List for the Lab Work

Chemicals:

No.	Description	Purpose
1.	Ferric chloride, $FeCl_3$	Synthesize the ionic liquid
2.	1-butyl-3-methylimidazolium chloride [BMIM]Cl	
3.	Nitrogen gas	
4.	4% and 6% BT in dodecane	Extraction

Equipments:

No.	Description	Purpose
1.	3-neck flask	Synthesize the ionic liquid
2.	Syringes (10ml)	
3.	Retort stand	
4.	Clamp for retort stand	
5.	Magnetic Stirrer	
6.	Glove bag with nitrogen tank connected	
7.	Vials	Store the ionic liquid and model oil
8.	Rotary machine	Extraction and analysis
9.	Lighter	
10.	Karl Fischer	
11.	FTIR	
12.	CHNS	
13.	Halogen Lamp	

Appendix C: Mass Calculation for $FeCl_3$ and [BMIM]Cl:

Reaction for synthesis [BMIM][$FeCl_4$]:

[BMIM]Cl	+	$FeCl_3$	→	[BMIM][$FeCl_4$]

One mole of [BMIM]Cl required one mole of $FeCl_3$ to produce [BMIM][$FeCl_4$] ionic liquid.

Molar Mass : [BMIM]Cl = 174.68 g/mol
: Anhydrous $FeCl_3$ = 162.21 g/mol
: $FeCl_3.6H_2O$ = 270.3 g/mol

$$\text{Mole} = \frac{\text{Mass}}{\text{MW}}$$

Desired Mole : 0.02 mole

Mass : [BMIM]Cl = 0.02 mole (174.68 g/mol)
= **3.493 g**
: Anhydrous $FeCl_3$ = 0.02 mole (162.21 g/mol)
= **3.244 g**
: $FeCl_3.6H_2O$ = 0.02 mole (270.3 g/mol)
= **5.406 g**

Appendix D: Calculation for Amount of Sulfur Removed from Model Oil (%)

Sulfur Removed from Model Oil (%) = Initial Sulfur Content (%) – Sulfur Remain in Model Oil (%)

- 4% Benzothiophene in dodecane after extraction with:

  Hexahydrates [BMIM] [$FeCl_4$]

  Sulfur Removed from Model Oil (%) = 3.125 – 0.379 = **2.746**

  Anhydrous [BMIM] [$FeCl_4$]

  Sulfur Removed from Model Oil (%) = 3.125 – 0.355 = **2.770**

- 6% Benzothiophene in dodecane after extraction with:

  Anhydrous [BMIM] [$FeCl_4$]

  Sulfur Removed from Model Oil (%) = 4.932 – 0.923 = **4.009**

Appendix E: Calculation for [BMIM][$FeCl_4$] Ionic Liquid Efficiency

$$\text{Ionic Liquid Efficiency} = \frac{\text{Initial sulfur content (\%)} - \text{Final sulfur content (\%)}}{\text{Initial sulfur content (\%)}} \times 100$$

- 4% Benzothiophene in dodecane after extraction with:

  Hexahydrates [BMIM] [$FeCl_4$]

  Efficiency (%) = $\frac{3.125 - 0.379}{3.125}$ x 100 = **87.87%**

  Anhydrous [BMIM] [$FeCl_4$]

  Efficiency (%) = $\frac{3.125 - 0.355}{3.125}$ x 100 = **88.64%**

- 6% Benzothiophene in dodecane after extraction with:

  Anhydrous [BMIM] [$FeCl_4$]

  Efficiency (%) = $\frac{4.932 - 0.923}{4.932}$ x 100 = **81.29%**

Appendix F: FTIR Correlation Table

Table below shows the IR absroptions for representative functional group retrived from http://www.chemistry.ccsu.edu/glagovich/teaching/316/ir/table.html

Functional Group	Molecular Motion	Wavenumber (cm^{-1})
alkanes	C-H stretch	2950-2800
	CH_2 bend	~1465
	CH_3 bend	~1375
	CH_2 bend (4 or more)	~720
alkenes	=CH stretch	3100-3010
	C=C stretch (isolated)	1690-1630
	C=C stretch (conjugated)	1640-1610
	C-H in-plane bend	1430-1290
	C-H bend (monosubstituted)	~990 & ~910
	C-H bend (disubstituted - E)	~970
	C-H bend (disubstituted - 1,1)	~890
	C-H bend (disubstituted - Z)	~700
	C-H bend (trisubstituted)	~815
alkynes	acetylenic C-H stretch	~3300
	C,C triple bond stretch	~2150
	acetylenic C-H bend	650-600
aromatics	C-H stretch	3020-3000
	C=C stretch	~1600 & ~1475
	C-H bend (mono)	770-730 & 715-685
	C-H bend (ortho)	770-735
	C-H bend (meta)	~880 & ~780 & ~690
	C-H bend (para)	850-800
alcohols	O-H stretch	~3650 or 3400-3300
	C-O stretch	1260-1000
ethers	C-O-C stretch (dialkyl)	1300-1000
	C-O-C stretch (diaryl)	~1250 & ~1120
aldehydes	C-H aldehyde stretch	~2850 & ~2750
	C=O stretch	~1725
ketones	C=O stretch	~1715
	C-C stretch	1300-1100
carboxylic acids	O-H stretch	3400-2400
	C=O stretch	1730-1700
	C-O stretch	1320-1210
	O-H bend	1440-1400
esters	C=O stretch	1750-1735
	C-C(O)-C stretch (acetates)	1260-1230
	C-C(O)-C stretch (all others)	1210-1160

acid chlorides	C=O stretch	1810-1775
	C-Cl stretch	730-550
anhydrides	C=O stretch	1830-1800 & 1775-1740
	C-O stretch	1300-900
amines	N-H stretch (1 per N-H bond)	3500-3300
	N-H bend	1640-1500
	C-N Stretch (alkyl)	1200-1025
	C-N Stretch (aryl)	1360-1250
	N-H bend (oop)	~800
amides	N-H stretch	3500-3180
	C=O stretch	1680-1630
	N-H bend	1640-1550
	N-H bend (1^o)	1570-1515
alkyl halides	C-F stretch	1400-1000
	C-Cl stretch	785-540
	C-Br stretch	650-510
	C-I stretch	600-485
nitriles	C,N triple bond stretch	~2250
isocyanates	-N=C=O stretch	~2270
isothiocyanates	-N=C=S stretch	~2125
imines	R_2C=N-R stretch	1690-1640
nitro groups	-NO_2 (aliphatic)	1600-1530 & 1390-1300
	-NO_2 (aromatic)	1550-1490 & 1355-1315
mercaptans	S-H stretch	~2550
sulfoxides	S=O stretch	~1050
sulfones	S=O stretch	~1300 & ~1150
sulfonates	S=O stretch	~1350 & ~1750
	S-O stretch	1000-750
phosphines	P-H stretch	2320-2270
	PH bend	1090-810
phosphine oxides	P=O	1210-1140